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## **Keywords**

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COLLEGE**

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BOMB REDUCTION OF THEIR FLUORIDES**

U N C L A S S I F I E D

ISC-688

U N I T E D   S T A T E S   A T O M I C   E N E R G Y   C O M M I S S I O N

Preparation of Zirconium and Hafnium Metals  
by Bomb Reduction of Their Fluorides

by

O. N. Carlson, F. A. Schmidt and  
H. A. Wilhelm

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Ames Laboratory  
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Preparation of Zirconium and Hafnium Metals  
by Bomb Reduction of Their Fluorides

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Abstract

A bomb process for preparing zirconium and hafnium metals with calcium by the reduction of their tetrafluorides is described. A detailed method of preparing the high purity tetrafluorides is presented and the purity and physical properties of the metals obtained are discussed.

Introduction

Experiments on the preparation of zirconium by bomb reductions have been described in reports by Walsh<sup>1</sup>, Peterson<sup>2</sup>, and Lambert et. al.<sup>3</sup> in 1950. These workers all employed the  $ZrF_4$  reduction with calcium, but Walsh alone employed zinc in the process. In this paper the preparation of zirconium and also of hafnium metal by a process similar to that of Walsh is described in detail.

Zirconium and hafnium metals are obtained in massive form as zinc alloys by the reduction of their tetrafluorides with calcium in the presence of zinc. The reaction which is sufficiently exothermic to yield liquid products is carried out

in a sealed bomb. The dense alloy which is immiscible with the molten slag phase separates as a homogeneous liquid. The zinc may later be removed from the solidified alloy by heating in a vacuum; this yields a sponge of the residual metal. Subsequent melting in a vacuum or inert atmosphere yields the pure zirconium or hafnium metal in massive form. Although hafnium so prepared is somewhat brittle, high quality, ductile zirconium can be obtained by this method.

Because of the importance of quality of the tetrafluorides to the success of this method, a detailed description is given for their preparation. In this investigation greater amount of the research and development work was done with zirconium. It was found that hafnium parallels zirconium quite closely in all processing steps, so less effort was required for this development.

The main properties which have been used by the authors to evaluate the quality of the zirconium metal obtained experimentally were its hardness and ability to be cold rolled. Generally, when the metal had a hardness of less than 50 Rockwell A, or 155 Brinell (3000 kg load), it was found to be readily fabricable by cold rolling. Since the effect of oxide impurity on the fabricability of zirconium is generally detrimental, the successful preparation of ductile zirconium metal depends largely upon the exclusion of oxygen from all materials and equipment used in processing.

### Preparation of High Purity Zirconium Tetrafluoride

Williams and Weaver<sup>4</sup> have prepared anhydrous zirconium tetrafluoride, free of significant amounts of oxygen by the hydrofluorination of zirconium oxide at 500°C followed by a vacuum sublimation of  $ZrF_4$  away from the unreacted oxide or oxyfluoride at 650°C. Hydrated zirconium tetrafluoride may be prepared by the reaction of aqueous hydrofluoric acid and zirconyl chloride octahydrate. This tetrafluoride may then be dehydrated in a stream of hydrogen fluoride gas at elevated temperatures to yield anhydrous zirconium tetrafluoride. In the work described here the latter process has been employed for preparing the tetrafluoride.

In this investigation zirconium chloride octahydrate was prepared from zirconium tetrachloride (hafnium free) obtained from the U. S. Bureau of Mines, Albany, Ore. The chloride was dissolved in distilled  $H_2O$  and this solution was then evaporated to a concentration of approximately 6 N in HCl, followed by cooling. Stirring the concentrated solution during cooling results in a crystalline deposit of  $ZrOCl_2 \cdot 8H_2O$  from which the excess liquid may be easily removed by filtration. These crystals can be further purified of iron by washing in acetone.

Aqueous HF (48-70 per cent) is added to the solid  $ZrOCl_2 \cdot 8H_2O$  resulting in the initial formation of a homogeneous liquid solution from which zirconium tetrafluoride monohydrate,  $ZrF_4 \cdot H_2O$ , is precipitated upon further addition of HF in accordance with the following reaction:





The supernatant liquid is approximately 7 N in hydrochloric acid, a concentration at which the solubility of the monohydrate is quite low. The use of more dilute hydrofluoric acid or aqueous solutions of zirconyl chloride decreases the acid concentration of the supernatant liquid and the yield of  $\text{ZrF}_4 \cdot \text{H}_2\text{O}$  crystals is decreased. The addition of excess hydrofluoric acid to the reaction mixture will likewise result in a decrease in the yield of  $\text{ZrF}_4 \cdot \text{H}_2\text{O}$  probably due to formation of the more soluble fluozirconic acid,  $\text{H}_2\text{ZrF}_6$ . Consequently, it is highly desirable to add essentially a stoichiometric amount of hydrofluoric acid. The addition of two or three drops of thorium nitrate solution to a few milliliters of the supernatant liquid determines the end-point. If a slight excess of fluoride ion is present the thorium nitrate forms a white precipitate of  $\text{ThF}_4 \cdot 2\text{H}_2\text{O}$ .

The mixture should be stirred continuously during the addition of the acid to help dissipate the heat evolved from the reaction and to aid in the formation of a granular crystalline precipitate. After cooling to room temperature the product can be filtered using plastic filtration equipment. The precipitate should then be dried in air at  $70^\circ\text{C}$  to yield a dry  $\text{ZrF}_4 \cdot \text{H}_2\text{O}$  product.

Anhydrous zirconium tetrafluoride may be obtained by dehydrating this monohydrate in a stream of dry hydrogen fluoride gas. It was found that this dehydration could be accomplished in a relatively short time in a heated rotating chamber. The

experimental equipment consisted of a monel tube inside of which was a magnesium cylinder for containing the monohydrate. This entire assembly was slowly rotated in an automatically controlled furnace.

A study was made of the temperature and time at which the water of hydration could be removed from 500 g batches of fluoride. Dehydration without pyrohydrolysis is essential in the drying of  $\text{ZrF}_4$ . It has been shown experimentally that an initial dehydration in a hydrogen fluoride atmosphere at 225-300°C is desirable for good grade tetrafluoride. The treatment removes about 80 per cent of the water of hydration in one to three hours. On the basis of several experiments a temperature of about 250°C has been selected for this initial drying step. At this temperature the hydrate undergoes considerable decomposition and the rate of pyrohydrolysis of the  $\text{ZrF}_4$  is exceedingly slow.

The remaining water can be readily removed by increasing the drying temperature. As can be seen from the data in Table 1 the hardness of the final metal is critically dependent upon the final drying temperature of the fluoride employed in its preparation. The higher hardness values of metal from some batches of the fluoride is believed to be due to the presence of greater amounts of  $\text{ZrOF}_2$  in the tetrafluoride. It is assumed that the rate of pyrohydrolysis to give  $\text{ZrOF}_2$  is much greater at the higher drying temperatures. On laboratory scale a drying treatment of 1 1/2 hours at 250°C followed by 2 1/2 hours at 400°C with constant rotation of the charge has been shown to give a fluoride that can be employed to give metal of high ductility. However, for larger scale drying operations the

practice has been to double the times at these temperatures.

Table I  
Dehydration of  $\text{ZrF}_4 \cdot \text{H}_2\text{O}$  in HF Atmosphere

Batch of $\text{ZrF}_4$	Initial Heating at 250°C Time (hrs.)	Final Heating of $\text{ZrF}_4$		Hardness of Zr Metal from the Batch of $\text{ZrF}_4$ Rockwell A
		Temp°C	Time(hrs.)	
1	2	400	2	48
2	3	400	5	48
3	3	450	5	51
4	1	500	7	55
5	2	550	6	70
6	2	600	6	71

Chemical analysis of a representative batch of zirconium fluoride dried at 250° and then at 400°C has shown it to contain 54.63 w/o Zr and 45.36 w/o F which is close to the theoretical  $\text{ZrF}_4$ . The common metallic impurities were found to be less than the following: 0.007 w/o Si, 0.003 w/o Cr, 0.002 w/o Mg, 0.004 w/o Ni, 0.002 w/o Cu, 0.002 w/o Ti, 0.025 w/o Fe, 0.002 w/o Ca and 0.003 w/o Al. A major source of the iron contamination is the 70% hydrofluoric acid which is received in steel containers. Use of higher purity hydrofluoric acid results in much lower iron contamination.

#### Preparation of $\text{ZrF}_4$ on Pilot Plant Scale

Several thousand pounds of  $\text{ZrF}_4$  have been prepared for research use in the Ames Laboratory as well as for other AEC

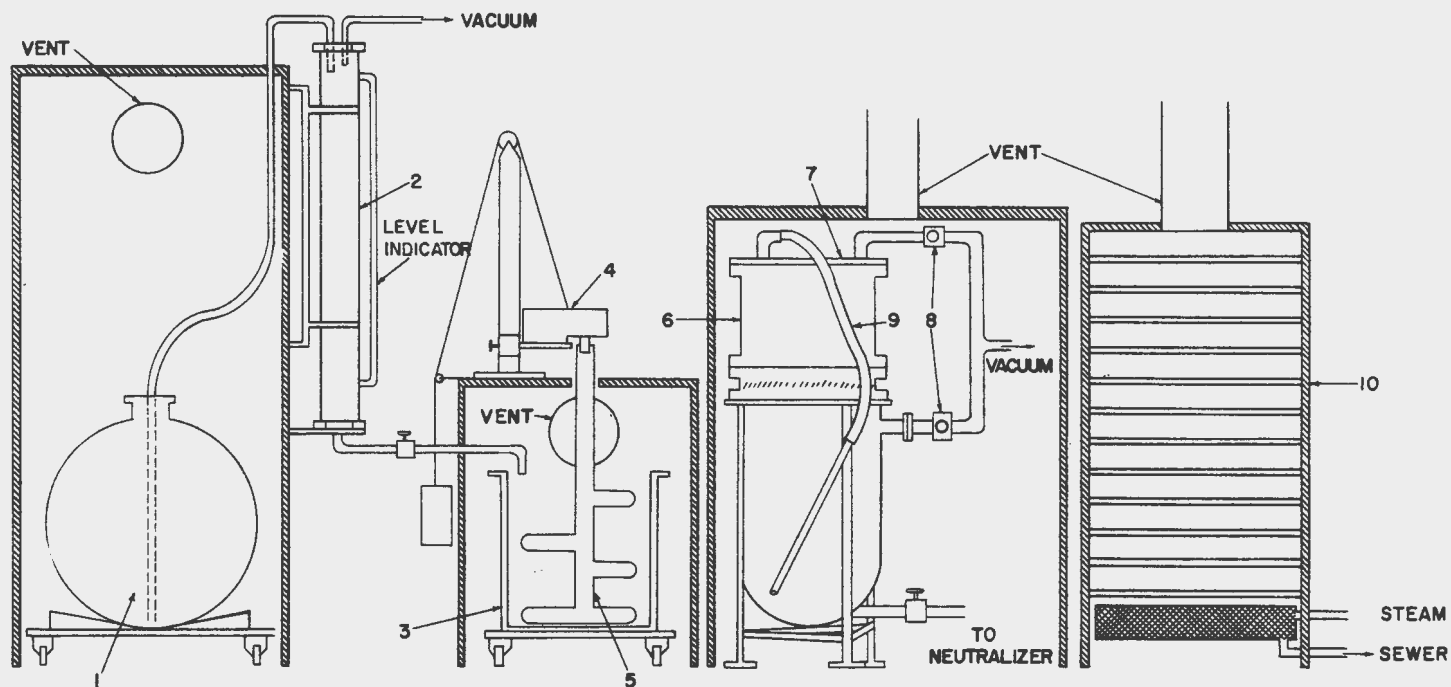
research laboratories. Pilot plant equipment was set-up for this operation with an output capacity of approximately 100 pounds of  $\text{ZrF}_4$  per individual batch. The procedure and equipment used for this scale of operation are described in detail in this section.

Zirconium tetrachloride, if in lump form, was dissolved directly in distilled water. Since the solution reaction is very exothermic and  $\text{HCl}$  is evolved, it was carried out by a slow addition of the lumps to the water in a ventilated area. In powder form, the chloride was introduced into the water by suction through a tube that extended below the surface of the water. About 50 pounds of  $\text{ZrCl}_4$  can be dissolved in 20 gallons of water but, if greater amounts than this are added, zirconyl chloride begins to crystallize out upon cooling. Either polyethylene-lined steel drums or glass-lined equipment may be used as solution vessels. Activated charcoal was added to the chloride solution to aid in filtering out the undissolved  $\text{ZrO}_2$  and carbon present in the tetrachloride. The filtrate was then concentrated by evaporation in a glass-lined steam-heated tank to a 6 N  $\text{HCl}$  concentration.  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  crystallized out upon cooling and this was filtered through a plastic-coated centrifugal filter.

Hydrofluorination of the  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was carried out in the equipment shown in Figure 1. The zirconyl chloride crystals were placed in the Kemplas reaction vessel (3) and aqueous 70% HF was transferred from the storage tank (1) into the metering unit (2) by means of a suction lift. The acid was then metered into the reaction vessel until a stoichiometric quantity had been added. Vigorous stirring is necessary during this reaction to assure an easily filterable product.

Transfer of the supernatant liquid and the  $\text{ZrF}_4 \cdot \text{H}_2\text{O}$  precipitate from the reaction vessel to the filter unit (6) was carried out by suction. A vacuum tight lid (7) was fitted over the top section of the filter unit and a vacuum drawn on the entire unit by opening both valves (8) to a steam operated aspirator. A flexible 1 1/2 inch diameter rubber tube with saran nozzle (9) connected to the lid of the filter unit was submerged in the reaction vessel sucking both the precipitate and the supernatant liquid into the top of the filter unit. A saran filter cloth placed over a perforated Kemplas filter plate at the junction of the two sections of the filter unit retained the solid and allowed the liquid to pass into the lower section of this apparatus. The filtration was speeded up by closing the top valve (8) and maintaining reduced pressure on the lower portion of the filtering unit.

The acid filtrate was discharged to the neutralizer and the wet precipitate was transferred to the steam heated dryer (10). After drying at  $70^\circ\text{C}$  for a few hours, the hydrated fluoride was



1. DRUM CONTAINING AQUEOUS HYDROFLUORIC ACID
2. SARAN PLASTIC METERING UNIT
3. KEMPLAS PLASTIC REACTION VESSEL
4. SLOW SPEED STIRRING MOTOR
5. SARAN PLASTIC STIRRER

6. KEMPLAS PLASTIC FILTER UNIT
7. VACUUM TIGHT LID
8. VALVES TO VACUUM LINE
9. RUBBER TRANSFER TUBE AND SARAN NOZZLE
10. STEAM HEATED DRYING OVEN

Fig. 1 - Precipitation and filtration equipment used in the preparation of  $\text{ZrF}_4 \cdot \text{H}_2\text{O}$ .

transferred to the equipment shown in Figure 2 for dehydration. Batches of about 100 pounds of fluoride were placed in the magnesium chamber (9) and the flange bolted in place on the iron furnace tube (8). This assembly extends through the electric resistance furnace (10) which has automatic temperature control. The HF gas line was connected and the furnace tube rotated slowly (about 20 revolutions per minute) while anhydrous HF from the cylinder (1) was passed over the powder. Horizontal fins inside the magnesium chamber increase agitation of the powder during rotation. A conical shaped trap (11) at the exit end of this chamber prevents excessive loss of material as dust in the exit gas stream. Dehydration of the monohydrate was carried out at 250°C for 3 hours and 400°C for 5 hours. The exit gases were scrubbed by a water spray (14) and passed into a neutralizing tank (15) where a soda ash neutralizing solution (16) was added. The other details of the diagram are control features and engineering details which are self-explanatory.

#### The Preparation of Zirconium Metal by the Calcium Reduction of the Tetrafluoride

Lambert, Hagelston and Hutchison<sup>3</sup> employed only iodine as an additive in their preparation of zirconium metal by bomb reduction. They reported that the metal thus obtained had a hardness of 88-90 R<sub>B</sub> (which is approximately 180 Bhn) and that it could be hot forged and subsequently cold-rolled with an overall reduction of 80 per cent. However, in the process presented here, zinc was added to the charge in order to form a

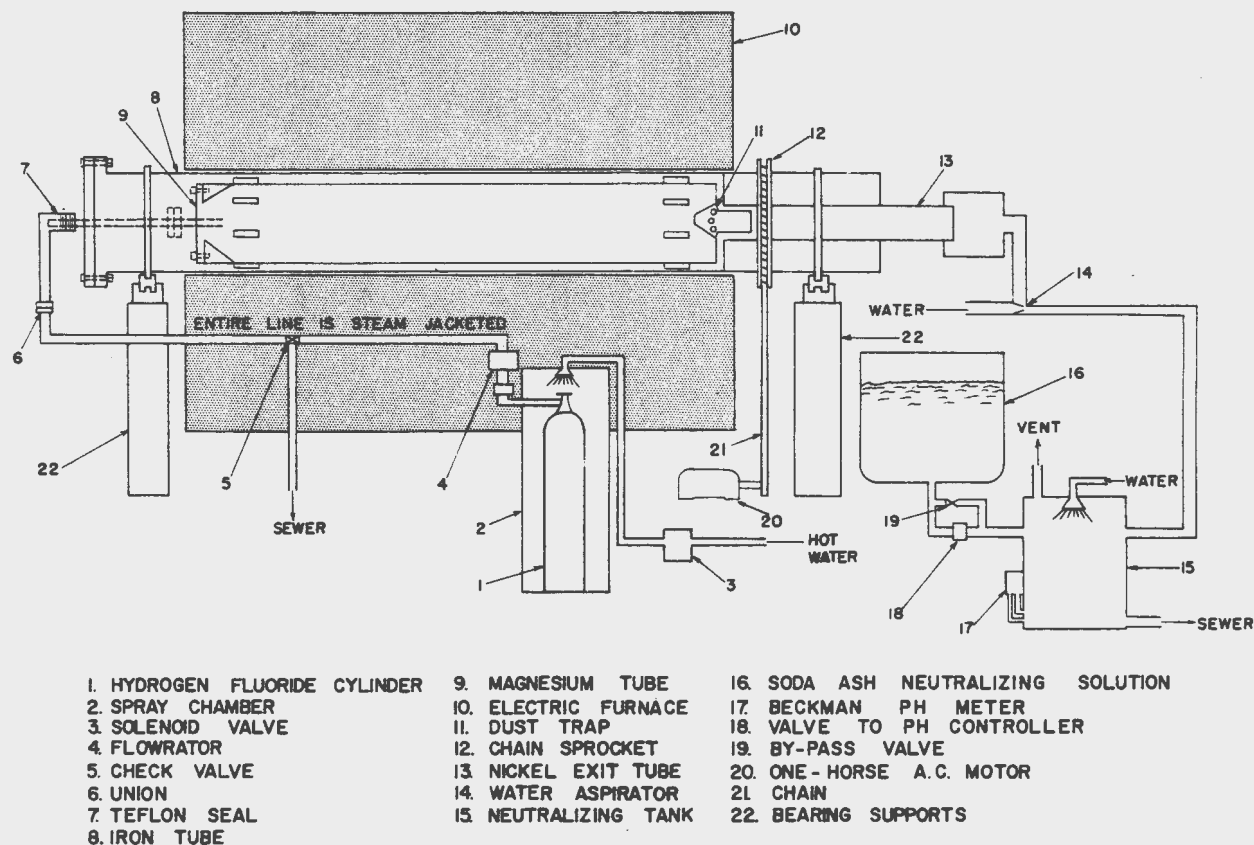


Fig. 2 - Furnace and rotary equipment used in dehydration of  $\text{ZrF}_4 \cdot \text{H}_2\text{O}$ .



low-melting alloy during the bomb reduction. Iodine was added to form calcium iodide which raised the temperature of the products and increased the fluidity of the slag. The zinc was subsequently removed almost quantitatively by heating in a vacuum up to  $1500^{\circ}\text{C}$ . This left a zirconium metal sponge which could be arc melted or melted in graphite to a dense ingot. This metal thus obtained had a hardness of 40-45  $R_A$  (120-135 Bhn) and was, with intermittent annealing, cold rolled to thin sheet.

The experiments described here were carried out in a steel bomb constructed from a 2 1/2 inch diameter steel pipe. One end of a 12 inch section of the pipe was closed by a welded-in plate; the other end, referred to as the top of the bomb, was threaded for a pipe cap. A refractory liner was inserted to prevent interaction between the charge and the bomb wall. The liner was either of a formed and pre-sintered type or was formed by jolting the refractory powder around a mandrel inside the bomb. The reaction was initiated either by placing the charged bomb in a gas furnace or by a hot wire ignition method. In the latter case a coil of suitable wire was embedded in the charge and a current passed through the wire to start the reaction.

The purity of the ingredients in the bomb charge, the ratios of zinc, of iodine, and of calcium to the zirconium fluoride, and the nature of the refractory liner are the major factors that determine the quality and yield of the final metal. The effects of these factors have been studied independently in numerous experiments by varying the amount or quality of each of the materials.

The addition of zinc to zirconium lowers its melting point quite markedly approaching a eutectic at  $1000^{\circ}\text{C}$  at approximately 33 w/o zinc. The percentage of zinc in the alloy has been shown to have a pronounced effect upon the quality of the final zirconium metal. Fig. 3 illustrates graphically the effect of varying the amount of zinc added as turnings to the bomb charge upon the hardness of the as-cast zirconium, other factors remaining constant. As can be seen from the figure, the addition of about 25 w/o zinc yields zirconium metal of lowest hardness. The alloy obtained with the 25% addition, actually contained, by chemical analysis, approximately 21 w/o zinc. The zirconium metal obtained from the alloy showed a hardness of Rockwell A 46.

The effect of the quality of the zirconium fluoride on the final metal hardness (described in a preceding section of this report) is equally pronounced.

Another factor which is recognized but not fully understood is the effect of the amount and quality of the calcium reductant. A calcium excess of at least 25 per cent over the stoichiometric amount appears to be a prerequisite in order to obtain ductile zirconium. The calcium used in these experiments was prepared by the authors by a vacuum redistillation of commercial calcium obtained from the New England Lime Co. The zirconium metal obtained with redistilled calcium was generally found to be soft although occasionally a batch of the redistilled calcium would consistently yield a harder zirconium. No correlation,

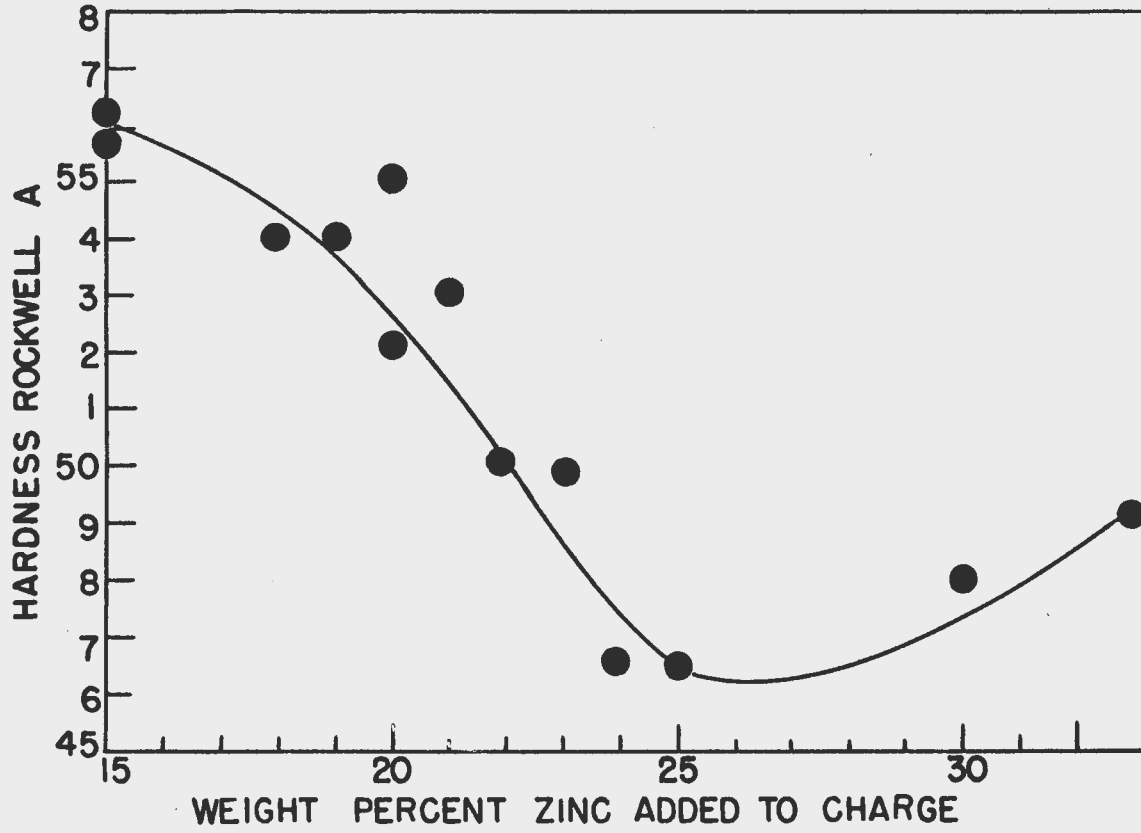


Fig. 3 - Zinc content of bomb charge vs hardness of zirconium after melting in graphite.

however, between the quality of the calcium and hardness of the resulting zirconium metal was found. Chemical analysis of the major impurities of a typical "good" batch of calcium showed less than the following amounts: 0.005 w/o iron, 0.004 w/o manganese, 0.003 w/o nitrogen, 0.001 w/o aluminum, 0.003 w/o carbon and 0.3 w/o magnesium.

The addition of a thermal booster is also essential in obtaining good yields and in producing good slag-metal separation. Although the amount of iodine added as a booster is not as critical as that of other constituents of the charge, the minimum quantity of booster required for good yields was studied and was found to vary in a manner dependent upon the size of the bomb. In a few experiments  $\text{ZnF}_2$  was substituted for both the zinc and iodine. Good yields were observed and metal of comparable quality was obtained when  $\text{ZnF}_2$  was used.

The liner material is also a potential source of oxygen contamination. Early work in which a few grams of  $\text{MgO}$ ,  $\text{CaO}$  and  $\text{ZrO}_2$  were added to individual reduction charges showed that  $\text{MgO}$  and  $\text{ZrO}_2$  additions resulted in greatly increased hardness of the zirconium whereas the  $\text{CaO}$  addition had relatively little effect. As a result of this and other experiments,  $\text{ZrO}_2$ ,  $\text{MgO}$  and dolomitic oxide were eliminated as suitable liner materials. Ductile zirconium was prepared using a liner of calcium oxide which was pre-fired to  $2000^\circ\text{C}$ . The results, however, were quite inconsistent, with some reductions resulting in ductile metal and others in quite brittle metal. Consequently  $\text{CaF}_2$  was

tried and was found to be much more satisfactory. Acid grade fluorspar, 97 per cent  $\text{CaF}_2$ , obtained from Ozark-Mahoning Company was used successfully and resulted in metal in consistently low hardness. Chief contaminants introduced by this liner were silicon, aluminum and nitrogen. Pretreating the  $\text{CaF}_2$  by leaching it in aqueous HF or by heating it in anhydrous HF at  $575^\circ\text{C}$ , reduced the contamination effects of these elements considerably.

A charge consisting of 350 g. of  $\text{ZrF}_4$ , 221 g. calcium, 64 g. zinc chips and 56 g. iodine was found to give ductile zirconium in yields of greater than 96 per cent when carried out under conditions pointed out above. Equally good results were obtained regardless of whether the charge was ignited by internal or external heating. Successful reductions were also carried out on a larger scale (one kilogram of  $\text{ZrF}_4$ ) employing a reduced ratio of the thermal booster.

The massive alloy obtained by the reduction reaction is referred to as a "biscuit". Figure 4 (a) shows a biscuit of the zirconium-zinc alloy obtained in the smaller scale reduction. The zinc can be removed from the alloy by heating it slowly in vacuo. At least ninety-five per cent of the zinc is readily removed at temperatures below  $1250^\circ\text{C}$ ; however, removal of the remaining zinc requires considerably longer time at  $1250^\circ\text{C}$  or higher temperatures. After heating to  $1500^\circ - 1600^\circ\text{C}$  in a graphite crucible, the sponge contains less than 0.05 w/o zinc but picks up some carbon. By use of a liner of zirconium sheet



**Fig. 4 - a). Zirconium-zinc alloy biscuit, as-reduced.  
b). Zirconium sponge after dezincing in vacuum  
showing considerable volume expansion  
resulting from rapid heating.  
c). Arc-melted button of zirconium.**

inside the graphite crucible it is possible to keep the carbon content of the sponge at less than 0.03 w/o. The remaining zinc is subsequently removed during the melting. Care must be taken in the dezincing procedure, since heating through the temperature range of 900 to 1250°C may result in too rapid evolution of zinc vapors with splattering and excessive expansion in the volume of the sponge, see Fig. 4 (b). A sample of arc-melted sponge zirconium is shown in Fig. 4 (c).

#### Properties of Bomb Reduced Zirconium Metal

Several pounds of zirconium metal sponge were prepared by the method described in the preceding sections. Some of the sponge was melted in a graphite crucible in vacuo and some arc melted under argon in conventional arc-melting equipment employing a tungsten electrode and a water-cooled copper pot. The hardness of the metal melted by either method was found to be in the range of 40-45  $R_A$  (120-135 Bhn with a 3000 Kg load). Zirconium thus prepared was cooled-rolled and, with intermittent annealing, fabricated into thin sheets of 10 mils thickness.

The lattice constants of bomb reduced and arc-melted zirconium were determined from x-ray diffraction patterns taken with a precision back-reflection camera. The values calculated by Cohen's analytical extrapolation method<sup>5</sup> were  $a = 3.234$  and  $c = 5.149 \text{ \AA}$ , which compare favorably with values of  $a = 3.232$  and  $c = 5.148 \text{ \AA}$  reported by Treco<sup>6</sup> for high purity crystal bar zirconium. The purity of zirconium metal prepared by

the bomb process and arc melted in an inert atmosphere was determined by chemical and spectrographic analysis. Representative amounts of the major impurities present in metal produced by this method are shown in Table II.

Table II  
Chemical Purity of Bomb-Reduced and Arc-Melted Zirconium Metal

Impurity	Weight %	Impurity	Weight %
Al	0.01	Mg	0.002
C	0.03	Mn	0.003
Ca	0.003	N	0.005
Co	0.001	Ni	0.003
Cr	0.003	O	0.1*
Cu	0.003	Si	0.02
Fe	0.02	Ti	0.001

\*The oxygen content of this metal has not been determined by vacuum fusion methods, but has been estimated as 0.10 to 0.15 w/o from Treco's<sup>6</sup> plot of hardness and lattice constants versus oxygen content.

The microstructure of a representative specimen of bomb-reduced and arc-melted zirconium is shown in the accompanying photomicrograph (See Fig. 5). The large equiaxed grains are a result of an annealing treatment.

#### Preparation of Hafnium Metal

The starting material for the hafnium preparation was a hafnium concentrate from a zirconium purification process. This



The bomb process and arc melted in an inert atmosphere was followed by chemical and spectrographic analysis. Representative analysis of the major impurities present in metal produced by this method are shown in Table II.

Table II

Chemical Analysis of Bomb-Reduced and Arc-Melted Zirconium Metal

Impurity	Weight %	Purity	Weight %
Al	0.01		
Si	0.02		
Ca	0.003		
Fe	0.001		
Cu	0.001		
C	0.001		
S	0.001		
P	0.001		

Fig. 5. Bomb-reduced zirconium metal, as-arc-melted. Annealed at 800°C and furnace cooled. Etchant: 1% HF in HNO<sub>3</sub>. 250X.

concentrate contained zirconium and hafnium in the ratio of approximately 1 to 24. Zirconium was removed from the hafnium by a liquid-liquid extraction method employing tributyl phosphate and an aqueous  $\text{HNO}_3$  solution of their oxychlorides.<sup>7</sup> The resulting hafnium contained less than 0.010 w/o zirconium. High purity hafnium hydroxide was precipitated from the aqueous phase, the hydroxide was redissolved in HCl and hydrated hafnium oxychloride was crystallized out of the solution. Aqueous hydrofluoric acid (70% HF) was added to these crystals to form hydrated hafnium fluoride. This material was dehydrated in a stream of hydrogen fluoride gas by the same method and temperature conditions described in the section on the preparation of zirconium fluoride.

The hafnium reduction step was also very similar to that for zirconium with slight modifications in the ratios of some of the ingredients in the charge. Zinc turnings were added to the charge in an amount calculated to give a hafnium alloy containing 21 w/o zinc. A representative charge for the experimental 2 1/2 inch diameter bomb consisted of 350 g  $\text{HfF}_4$ , 275 g  $\text{I}_2$ , 192 g Ca and 65 g Zn. A number of reductions were also made in a six-inch bomb in which 16 pound biscuits of hafnium-zinc alloy were obtained. The zinc was removed by heating slowly in a graphite crucible under vacuum to 1800°C. An overall yield of 97 per cent hafnium metal was obtained from the reduction and dezincing steps. The resulting sponge was analyzed chemically and spectrographically and the principal impurities are shown in Table III.

Table III

## Chemical Purity of Bomb-Reduced Hafnium Sponge

<u>Element</u>	<u>Weight %</u>
Calcium	less than 0.01
Iron	less than 0.01
Magnesium	less than 0.01
Silicon	less than 0.01
Zinc	less than 0.002
Zirconium	less than 0.01
Carbon	0.07
Nitrogen	0.05
Oxygen	not determined

Although the oxygen content of the sponge was not determined, it is undoubtedly present in considerable amounts as indicated by the extreme brittleness of the material.

Most of this sponge was sent to the Foote Mineral Company for further purification by the iodide process. The dense crystal bar metal obtained by this processing treatment was analyzed chemically and found to have undergone significant reduction in the carbon (0.03 w/o) and nitrogen (0.009 w/o) content. Some of the sponge hafnium was arc-melted directly and a few of its physical properties were compared with those of the crystal bar hafnium as shown in Table IV.

Table IV

Comparison of Physical Properties of Sponge and Iodide Hafnium

	<u>Hafnium Sponge As-arc Melted</u>	<u>Hafnium Crystal Bar As-arc Melted</u>
Melting Point, °C	2235	2150
Hardness, ( $R_A$ )	69	60
Lattice Constants (Å)		
a	3.199	3.197
c	5.072	5.057
c/a	1.585	1.582
Density (g/cc)		
Measured	13.19	13.29
Calculated from x-ray data	13.19	13.25

The microstructure of the arc melted sponge is shown in Fig. 6 and of the arc melted crystal bar in Fig. 7.

#### Summary

A practical process was developed for the preparation of zirconium and hafnium metals. The method entails a bomb reduction of  $ZrF_4$  or  $HfF_4$  with calcium to form a massive zinc alloy. The zinc was removed by heating in vacuum to yield a sponge of zirconium or hafnium metal.

Zirconium and hafnium tetrafluorides can be prepared in high purity by an aqueous reaction to form the hydrated fluorides which are subsequently dehydrated at elevated temperatures in an atmosphere of HF gas. Extensive studies were made of the

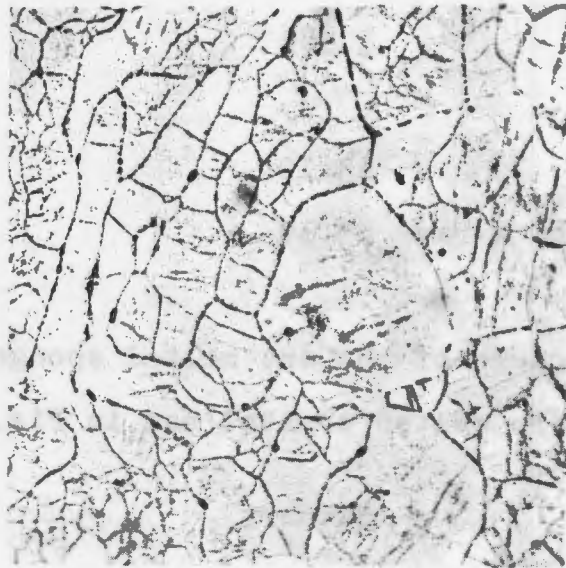


Fig. 6. Bomb-reduced hafnium metal, as-arc-melted.  
Etchant: 1% HF in  $\text{HNO}_3$ . 250X.



**Fig. 7.** Crystal bar hafnium metal, as-arc-melted.  
Etchant: 1% HF in  $\text{HNO}_3$ . 250X.

conditions for the preparation of high purity zirconium tetrafluoride and pilot plant equipment is described which was used to prepare 100 pound batches of the fluorides.

The reduction step was investigated thoroughly, particularly for zirconium, and those factors which affect metal quality and yield were determined. Reduction yields of 96 per cent were obtained with both zirconium and hafnium. After arc-melting, the sponge zirconium had a hardness of 40-45 Rockwell A and was readily cold-rolled into sheet. Zirconium metal thus prepared had a purity of about 99.8 per cent.

Hafnium metal, similarly prepared, had a hardness of 69 Rockwell A and was hot-rolled but was too brittle to be easily cold worked. The hafnium was low in metallic impurities, but contained considerable amounts of carbon, nitrogen and oxygen.

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